Phase Transitions: Diversity in dynamics

Subir K. Das
Jawaharlal Nehru Centre for Advanced Scientific Research
Bangalore

Works done/ contd. with

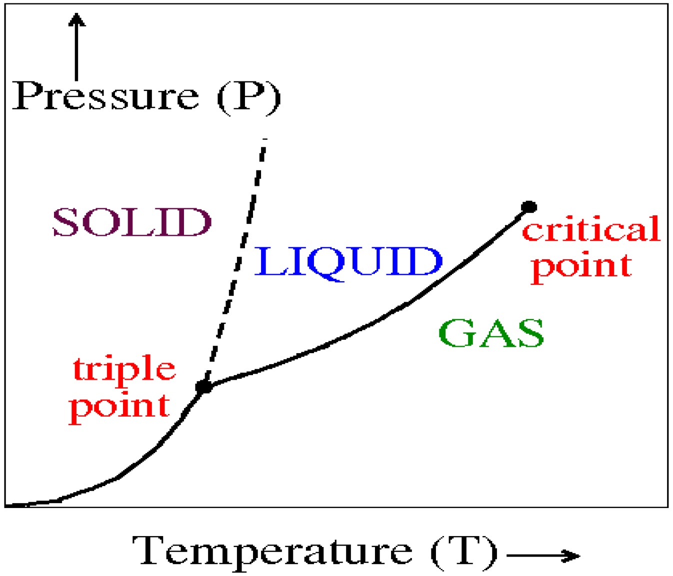
- Jiarul Midya
- Nalina Vadakkayil
- Sutapa Roy
- Subhajit Paul

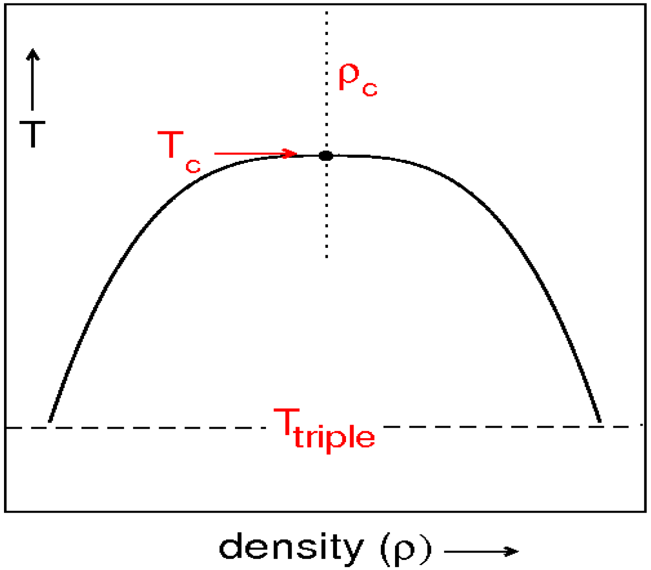



Plan:

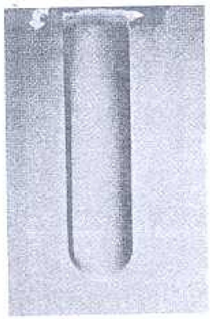
- Introduction:
  Phase Transitions
  – A general overview of Universality
- Results for
  Nucleation and Growth in
  vapor-liquid and vapor-solid phase transitions
- Conclusion

Phase Transitions and Critical Phenomena

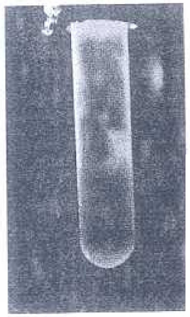




$T \gg T_c$



$T \simeq T_c$



$T \ll T_c$

J.V. Sengers & others

Critical phenomena is about order parameter fluctuation

Order parameter $\varphi = \rho - \rho_c ; \rho_l - \rho_v$

Structure of fluctuation: $C(r) = \langle \varphi(\vec{r}) \varphi(\vec{0}) \rangle - \langle \varphi(\vec{r}) \rangle \langle \varphi(\vec{0}) \rangle$

$$C(r) = r^{-p} \exp(-r/\xi) \qquad p = d - 2 + \eta$$

Correlation Length ξ : correlated distance, central quantity

$\xi = \xi_0 \epsilon^{-\nu}$ a measure of fluctuating length $\qquad \epsilon = (T - T_c)/T_c$

M.E. Fisher, Rep. Prog. Phys. (1967)

Phase Transitions and Critical Phenomena

$$\varphi = B\epsilon^{\beta} \qquad \chi = X_0 \epsilon^{-\gamma} \qquad C = C_0 \epsilon^{-\alpha}$$

$$C(r) = r^{2-d-\eta} \exp(-r/\xi) \qquad \xi = \xi_0 \epsilon^{-\nu}$$

Scaling relations

Rushbrooke $\alpha + 2\beta + \gamma = 2$

Fisher $(2-\eta)\nu = \gamma$

Josephson $\nu d = 2 - \alpha$

Hypothesis: A dimensionless quantity will be invariant and others will change according to their dimensions & near the critical point ξ is the only characteristic length.

Landau, …, Fisher, Widom, Kadanoff, Wilson, ...

Universality

Values of the exponents are universal: depend upon dimensionality, order parameter symmetry and range of interaction, do not depend on the material and type of transition. The universality is rather robust.

d=3, scalar order parameter

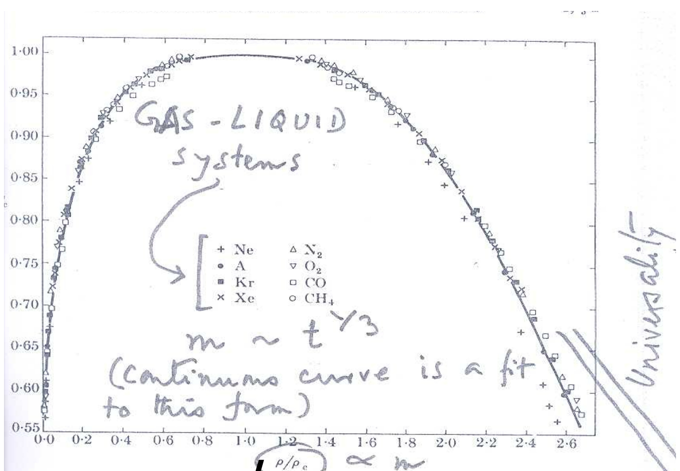
Ising Class: Interaction short ranged, decays faster than $1/r^d$

$$\beta=0.325, \gamma=1.239, \alpha=0.11, \nu=0.63$$

Classical Universality Class: Interaction decays slower than $1/r^d$

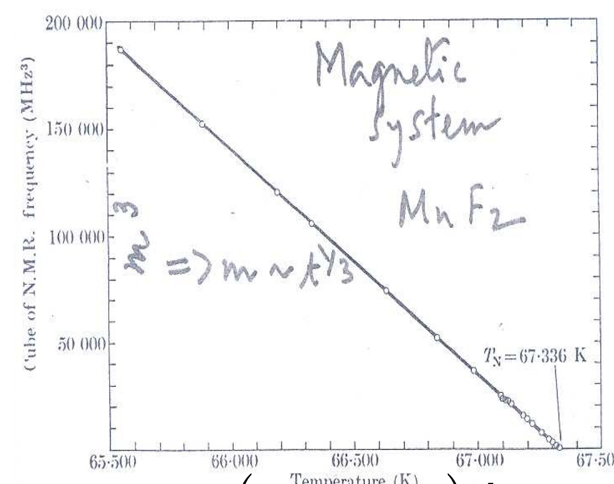
$$\beta=1/2, \gamma=1, \alpha=0, \nu=1/2$$

T/T_c



$\rho/\rho_c \propto \varphi$

φ^3



$\epsilon=(T_c-T)/T_c$

Microscopic details are not important: inherent in the Renormalization Group Theory

Critical Slowing Down of Fluctuations

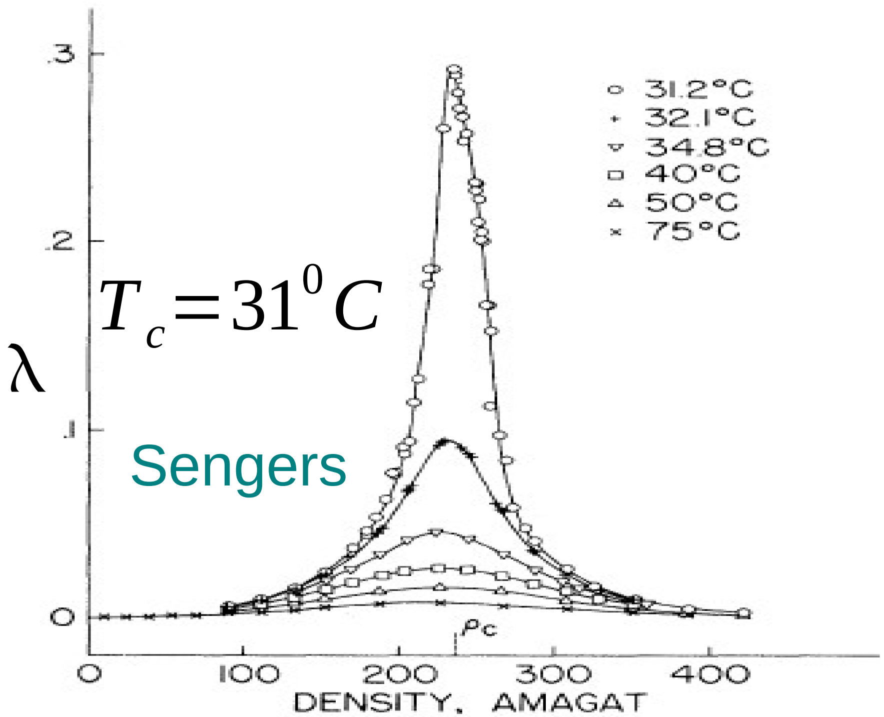
Classical van Hove Theory

At criticality dynamics is driven by statics

$$S(q,t)=S(q,0)\,e^{-D_T q^2 t}\,;\,D_T=\frac{\lambda}{K_T}$$

$K_T \rightarrow \infty,\ \lambda$ finite

$D_T \rightarrow 0$ as K_T^{-1}



Stokes-Einstein-Sutherland relation:

$$D_T=\frac{R_D k_B T}{6\pi\eta(T)\xi(T)}$$

$$\eta \sim \xi^{x_\eta}\,;\,D_T \sim \xi^{x_D}\,;\,x_D=1+x_\eta$$

$$x_\eta=0.068\,;\,x_D=1.068$$

$$z=2+x_D\,;\,\tau \sim \xi^{z}$$

Mode Coupling theory,
Dynamic Renormalization Group theory
(Kawasaki, Hohenberg, Ferrell, Bhattacharya, Sengers)

Verified by experiments
(Sengers & coworkers, ...)

Critical Slowing Down of Fluctuations

$$x_\eta = 0.068\,;\, x_D = 1.068\,;\, x_\zeta = 2.89$$

K. Jagannathan and A. Yethiraj, Phys. Rev. Lett. 2004

A. Chen, E.H. Chinowitz, S. De and Y. Shapir, Phys. Rev. Lett. 2005

SKD, M.E. Fisher, J.V. Sengers, J. Horbach, K. Binder, Phys. Rev. Lett. 2006

S. Roy and SKD, Europhys. Lett. 2011

S. Roy, S. Dietrich and F. Hoefling, J. Chem. Phys. 2016

J. Midya and SKD, J. Chem. Phys. 2017

$$\tau \sim \xi^z; \quad z = 2 + x_D$$

Finite-size scaling: $\tau \sim L^z$
M.E. Fisher (1971)

Para-to-ferromagnetic transition: $z \simeq 2$

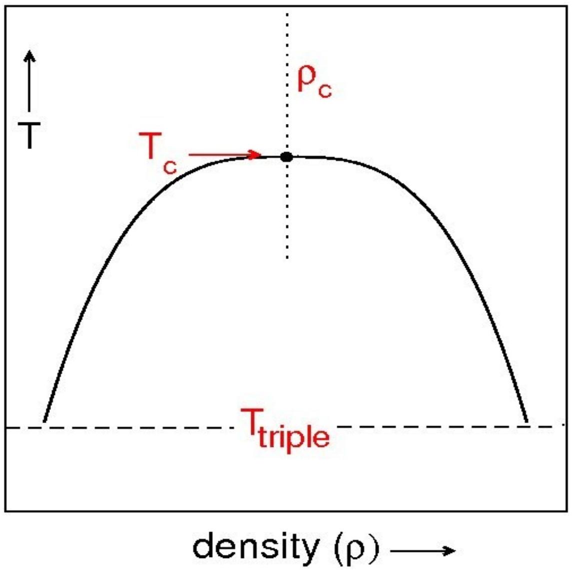
Fluid-fluid transition: $z \simeq 3$

Weaker universality in dynamics than in statics.

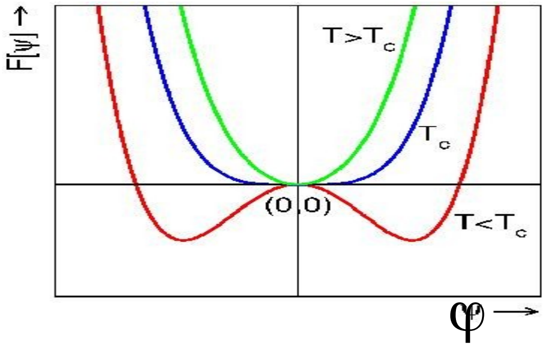
Phase separation in solid binary mixtures: $z \simeq 4$

D.P. Landau and K. Binder, Monte Carlo Simulations …, Cambridge ... (2009)

Kinetics



Order parameter $\varphi \equiv \rho - \rho_c$

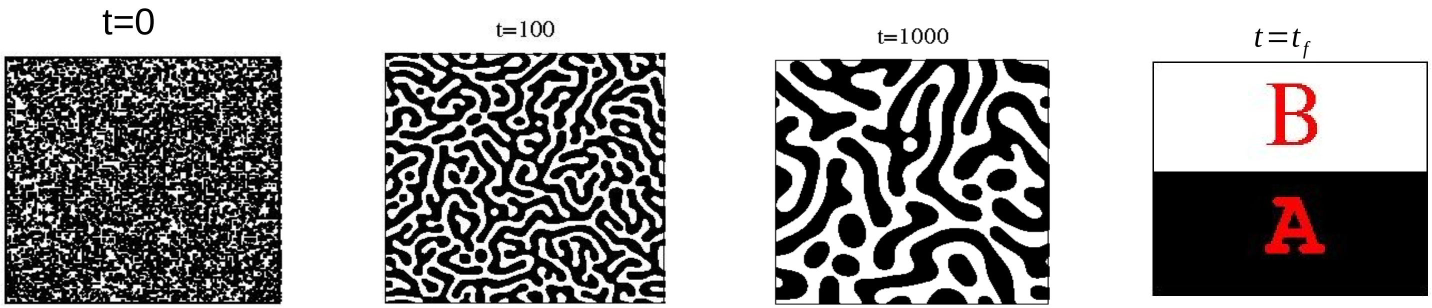


High $T, \varphi = 0$; Low $T, \varphi \neq 0$

Free energy minima at equilibrium values of ψ

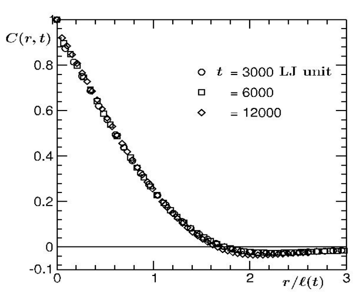
$$F(\varphi) = (T - T_c)\varphi^2 + \varphi^4$$

--Landau Free energy.



Quench inside the coexistence curve; systems out of equilibrium; phase separation via formation and growth of particle rich (poor) regions.

$$C(r,t) = \langle \varphi(\vec{r},t)\varphi(\vec{0},t)\rangle - \langle \varphi(\vec{r},t)\rangle\langle \varphi(\vec{0},t)\rangle$$



Self-Similar Structure

$$C(r,t) \equiv C(r/\ell(t))$$

Recall:

$$\ell(t) \sim t^{\alpha} \qquad (\tau \sim \xi^z)$$

Like critical phenomena

Universality?

A.J. Bray, Adv. Phys. (2002); S. Puri & V. Wadhawan, Kinetics of Phase Transitions, CRC (2009).

Coarsening Phenomena: $\ell(t) \sim t^{\alpha}$ Like critical phenomena: $t \rightarrow 1/\epsilon$

Universality?

Ordering in ferromagnets: $\alpha = 1/2$

Phase separation in solid mixtures: $\alpha = 1/3$

Phase separation in liquid mixtures: depends upon morphology

Percolating: $\alpha = 1/3, 1, 2/3$ Disconnected: $\alpha = 1/3$

Vapor-liquid phase separation: … morphology

Percolating: $\alpha = 1/3, 1, 2/3$ Disconnected: $\alpha = 1/3$

Vapor-solid phase separation: should depend upon morphology

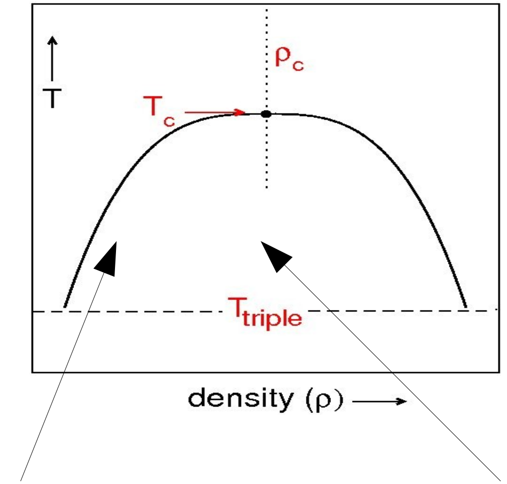
Liquid-solid phase separation: $\alpha = ?$

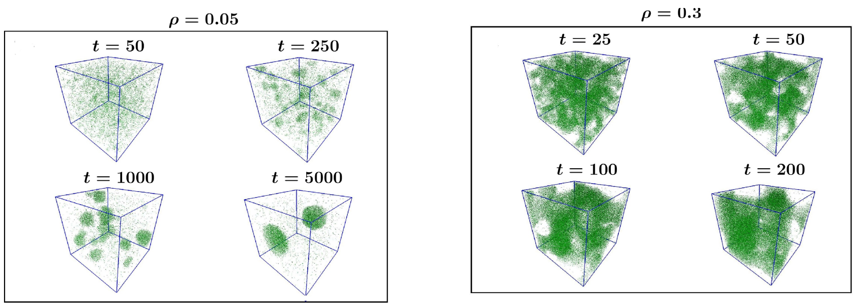
Lifshitz, Cahn, Allen, Slyozov, Binder, Siggia, Furukawa

First Order Transitions – more varieties.

FOCUS: Disconnected, vapor-liquid & vapor-solid transitions – NUCLEATION & GROWTH

- Typically people draw another boundary inside the coexistence curve --- <u>spinodal line</u>
- Inside the spinodal boundary the system becomes unstable to small fluctuations – kinetics is referred to as spinodal decomposition
- Outside the spinodal region the system is in metastable state and phase separation happens via nucleation and growth





<u>Examples of Nucleation</u>

1. Crystallization in liquid

2. Formation of cloud droplets around cloud condensation nuclei

3. Formation of microfilament in biology (binding of actin molecules)

4. Formation of bubbles in a cocacola bottle

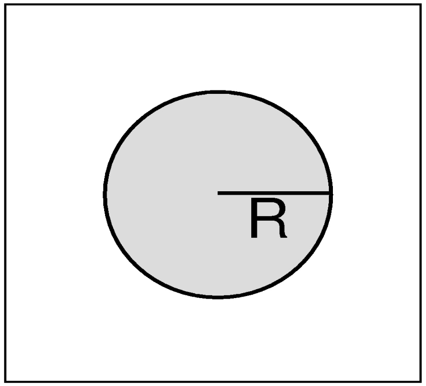
5. Nucleation of quark-gluon plasma, hadronic composite

6. Accumulation of cosmic dust to form planets, etc.

<u>What is Nucleation?</u>

Nucleation

Formation of embryo/nucleus with the introduction of boundary between two phases.



E.g., from a slightly over-saturated vapor, a liquid droplet forms being separated from the gas background by an interface
---- Vapor-Liquid Transition

Relevant in cloud nucleation.

NOTE: Presence of interface introduces (free) energy Barrier.

Types: a) Homogeneous Nucleation
b) Heterogeneous Nucleation

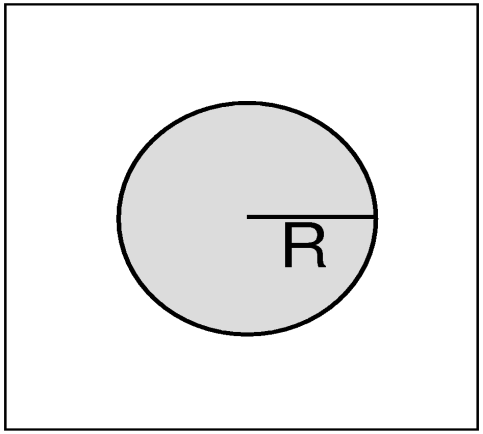
Some References:

K. Binder, Rep. Progr. Phys. 50, 783 (1987)
P.G. De Gennes, Rev. Mod. Phys. 57, 827 (1985)
M. Schick, in Liquids at Interfaces (Amsterdam, 1990)
J.S. Rowlinson and B. Widom, Molecular Theory of Capilarity (Oxford, 1982)

Homogeneous Nucleation: Classical Picture

Nucleation can occur due to gain in free energy in the new phase

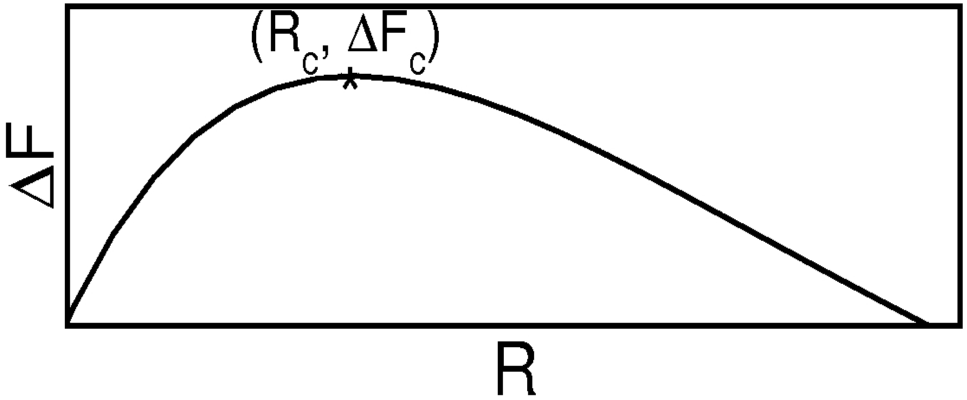
At the same time energy penalty comes due to the formation of interface.



Required free energy for the creation of a spherical droplet of radius R

$$\Delta F(R) = -\frac{4}{3}\pi R^3 \delta F_v + 4\pi R^2 \gamma$$

Bulk (B) Surface (S)



$$R < R_c : \frac{dF}{dR} > 0$$

→ There is cost of adding particles to the droplet

$$R > R_c : \frac{dF}{dR} < 0$$

→ There is energy gain due to addition of particles

Problems of interest: $R_c, \Delta F_c, \gamma,$ Nucleation Rate, Growth, etc.

$R = R_c$: Critical radius = $\frac{-2\gamma}{\delta F_v}$ $\left(\frac{d\Delta F}{dR} = 0\right)$ $\Delta F_c = \frac{16\pi\gamma^3}{3\delta F_v^2}$

Rate of nucleation $\propto$ Boltzmann Factor $exp(-\Delta F_c / k_B T)$ Arrhenius

Classical Nucleation Theory: $F_s = 4\pi R^2 \gamma$ $\gamma =$ constant

In reality: $\gamma = \gamma(R)$

R.C. Tolman (1949): $\gamma(R) = \frac{\gamma}{1 + 2\delta / R}$ $\delta \rightarrow$ Tolman Length

Fisher and Wortis (1986): $\gamma(R) = \gamma / (1 + 2\frac{\delta}{R} + 2(\frac{l_0}{R})^2)$

Anisimov; Das and Binder: Critical behavior of $\gamma(R)$

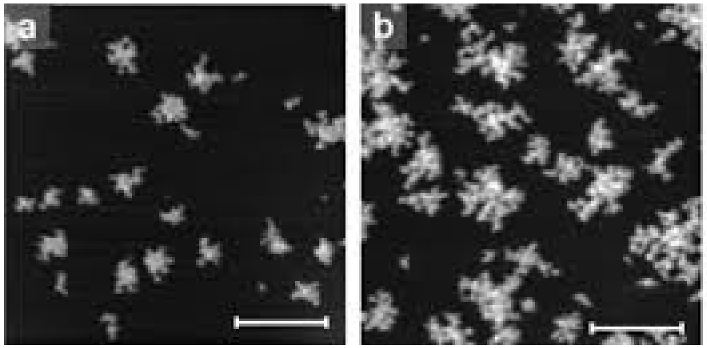
$$\gamma(R)\xi^2 = \frac{C_1}{1 + C_2(\frac{\xi}{R})^2}$$

SKD and K. Binder, Phys. Rev. Lett. (2011)

SKD, Molecular Simulations (2015)

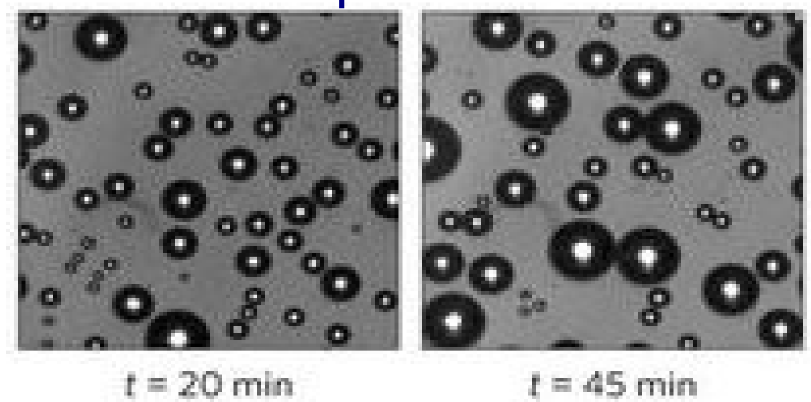
Growth: Possible ways in disconnected morphology

Ice



Heidom et al. (CPL)

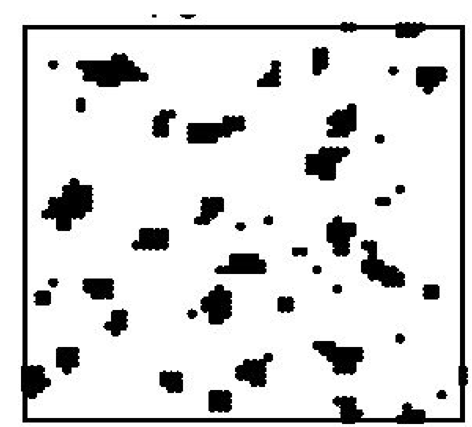
Liquid water



Mouterde et al. (Nature Materials)

Droplets consist of small particles.

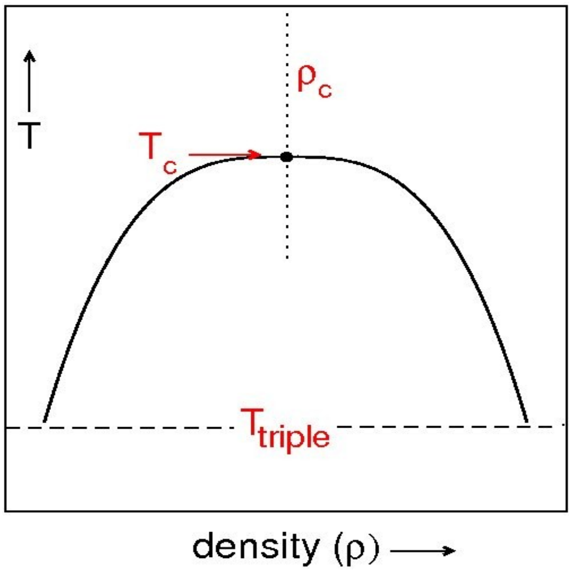
Particles from smaller droplets get detached to be deposited on a bigger droplet.



Droplets **themselves move** and undergo ``sticky Collisions'' with each other to form bigger droplets.

Motion of droplets/clusters can be diffusive, ballistic, … .

Kinetics of phase separation close to the coexistence curve



Solid-solid $(\rho \rightarrow x_\alpha)$ Ostwald ripening-
particle diffusion

Wilhelm Ostwald (1896)

$$\frac{d\ell(t)}{dt} \sim |\nabla \mu| \sim \frac{\gamma}{\ell(t)^2} \rightarrow \alpha = 1/3$$

--Lifshitz-Slyozov (1961).

Liquid-Liquid $(\rho \rightarrow x_\alpha)$ Droplet diffusion and coalescence mechanism

$$\frac{dn}{dt} = -C n^2 \qquad C = D\ell = constant \qquad n \propto 1/\ell^d \qquad \ell \sim t^{1/d}$$

K. Binder and D. Stauffer(1974) E. Siggia (1979)

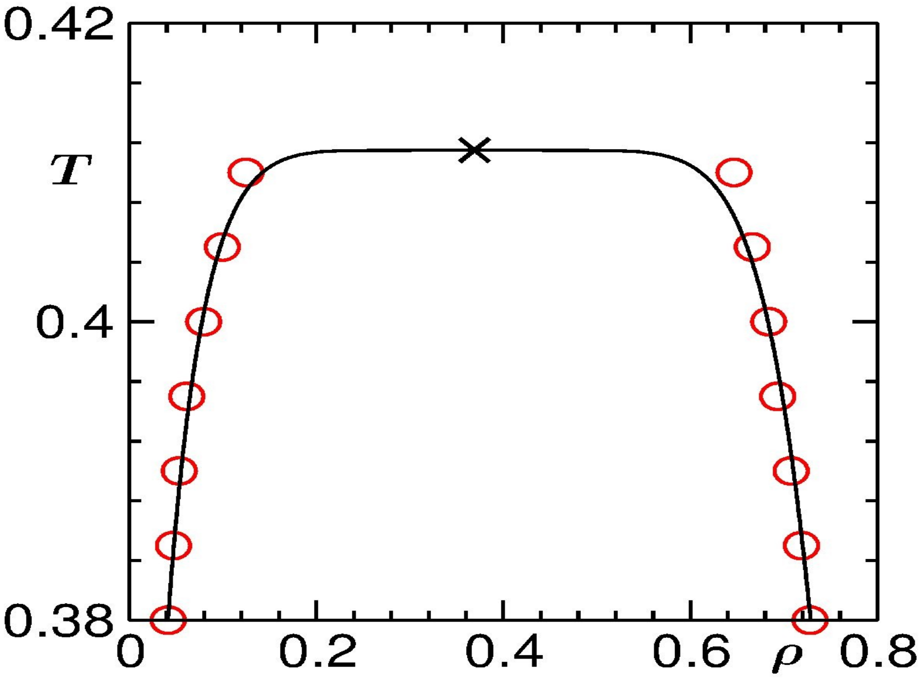
Vapor-Liquid – high vapor density, droplet diffusion picture may still apply

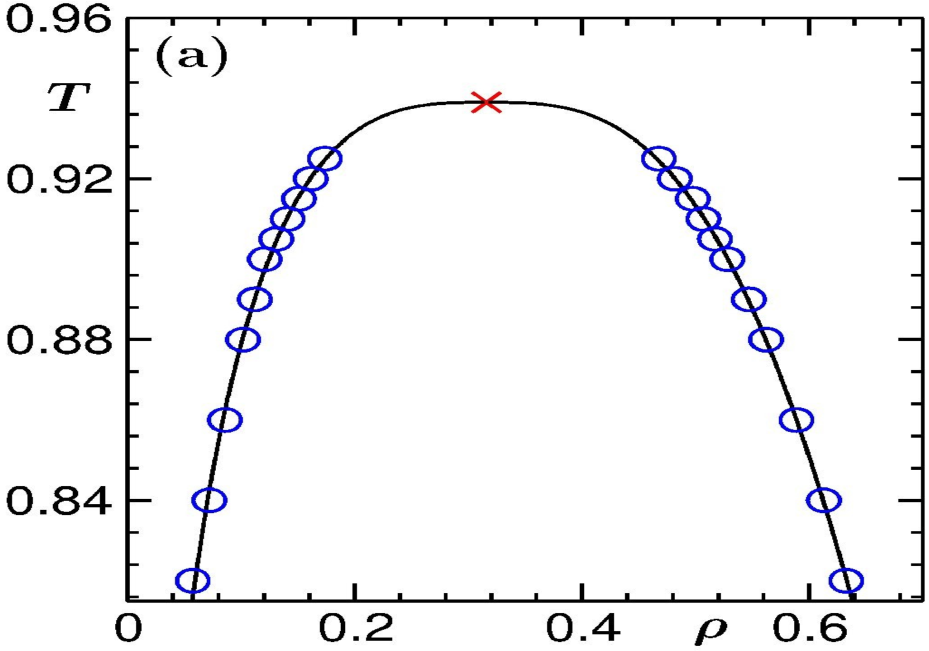
Vapor-Solid – with very low vapor density, motion of solid droplets may be ballistic – ballistic aggregation picture

Typically one uses Model H, Lattice Boltzmann, Molecular Dynamics

Our Model: $$\varphi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$ LJ potential + truncation, shift, force correction.

Phase behavior: Monte Carlo simulations





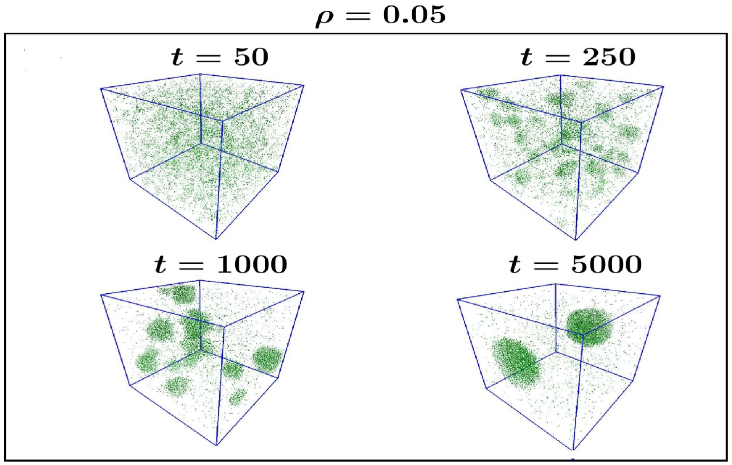
J. Midya and SKD: J.Chem. Phys. (2017)
J. Chem. Phys. (2017)

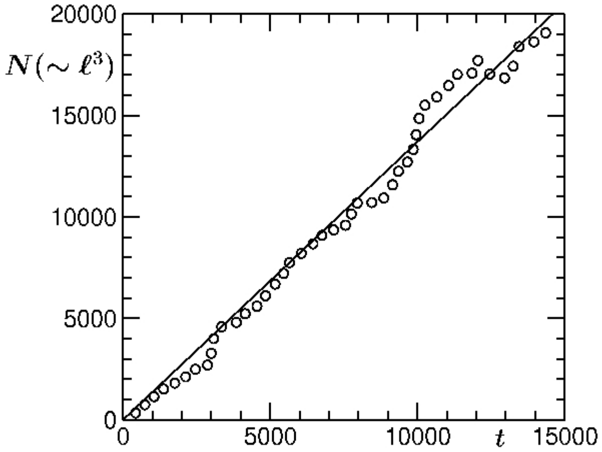
Kinetics: Molecular dynamics simulation with Nose-Hoover thermostat

Nucleation and Growth in vapor-liquid phase separation in d=3

S. Roy and SKD (3D): Physical Review E R(2012); Soft Matter (2013)
Journal of Chemical Physics (2013)

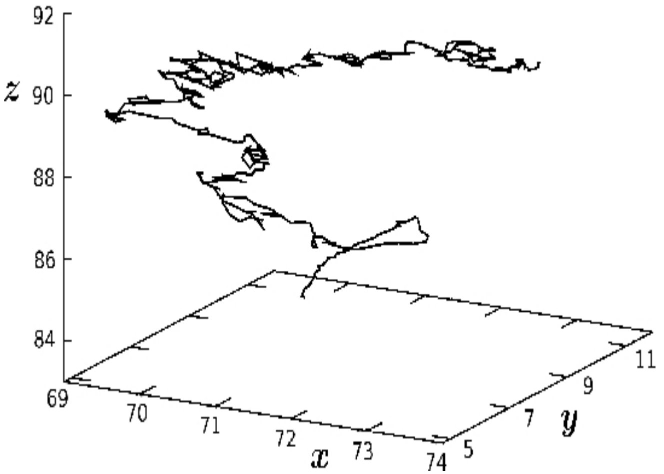
J. Midya and SKD (2D): J. Chem. Phys. (2017)





Pattern consists of spherical droplets

Droplets exhibit random motion



Droplet diffusion and collision mechanism of Binder and Stauffer

$$dn/dt = -D\,\ell\,n^2 \qquad 1/n \sim t$$

$$n \propto 1/\ell^3 \qquad \ell \sim t^{1/3}$$

Binder and Stauffer (1974)

Siggia (1979)

Ballistic aggregation: Materials Science, Granular Matter, Astrophysics, … .

Carnevale et al., PRL (1990).
Trizac and Krapivsky, PRL (2003).

Hansen and Trizac, JSP (1996).
J. Blum, Astron & Astroph (2010).

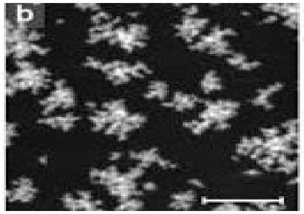
2 types:

Ballistic deposition – seed is fixed (vapor deposition on a substrate, etc.).

Source: ERCIM

Ballistic aggregation: all clusters move (translation and rotation) and collide.

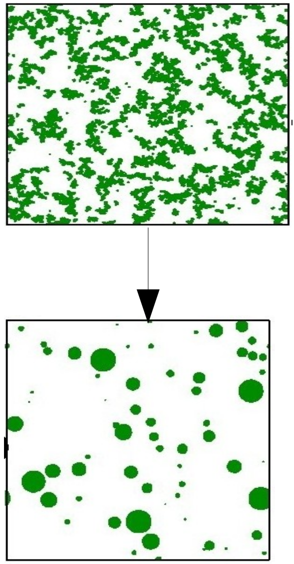
shutterstock.com



Heidom et al. (CPL)

Fractality is usually a natural outcome.

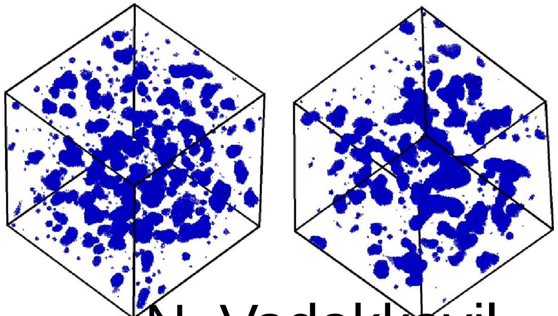
Typical simulations are with ``sticky'' hard spheres – fractal structures are expected.



In event driven simulations, it's necessary to keep track of exact locations as well as orientations of fractal clusters and identify exact points of contact during collision – technically challenging – so Spherical cluster approximation becomes necessary.

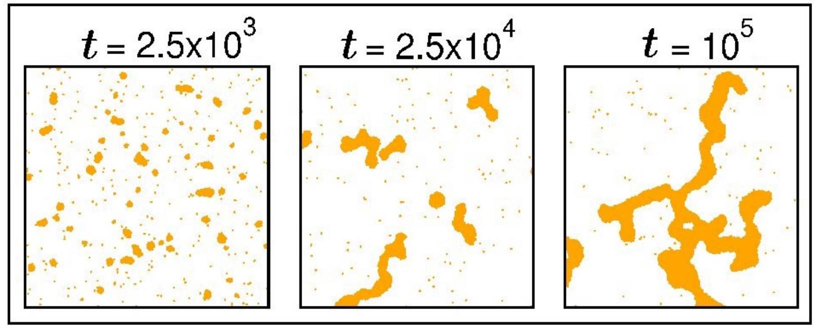
Kinetics of vapor-solid transition

facts from molecular dynamics simulation of the Lennard-Jones model.

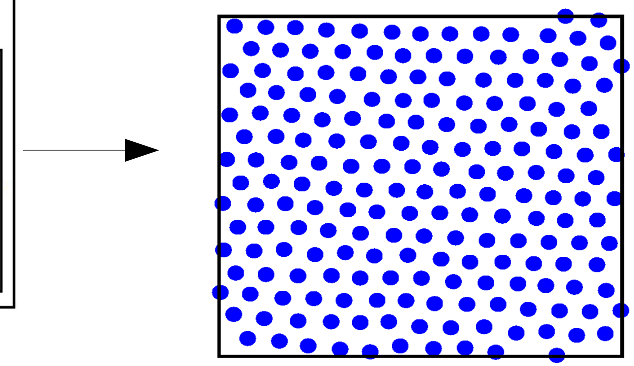


N. Vadakkayil

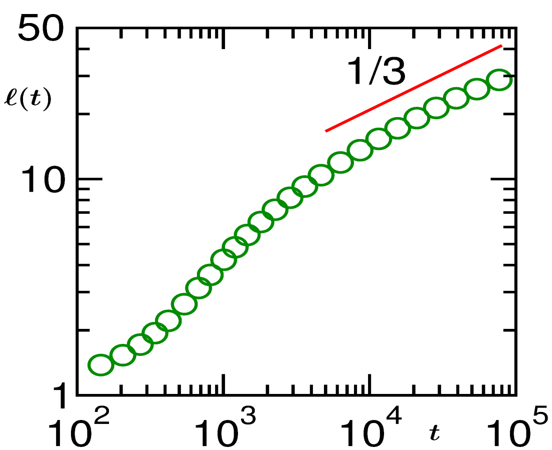
S. Roy



J. Midya

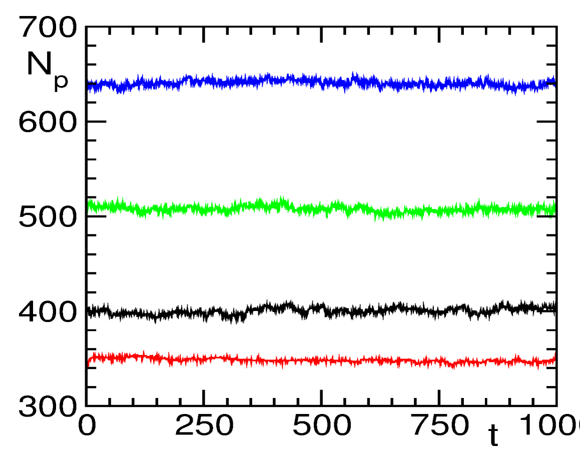


After the collisions, because of crystalinity, constituent particles do not get enough time/cannot move much to give the cluster a circular shape, before another collision occurs – FRACTALITY.



$$\ell \sim t^{1/3}$$

Ostwald ripening?



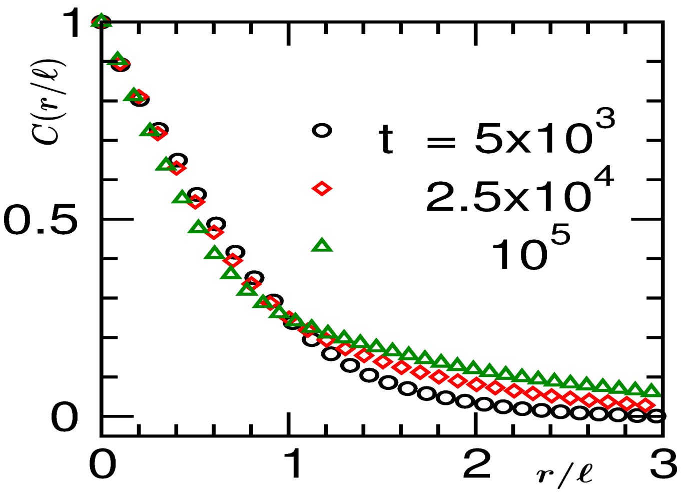
Between two collisions, no. of particles inside droplets remain constant--- NOT Ostwald ripening. – Coalescence Mechanism.

But for diffusive coalescence mechanism in d=2: $\ell \sim t^{1/2}$???

Kinetics of vapor-solid transition –

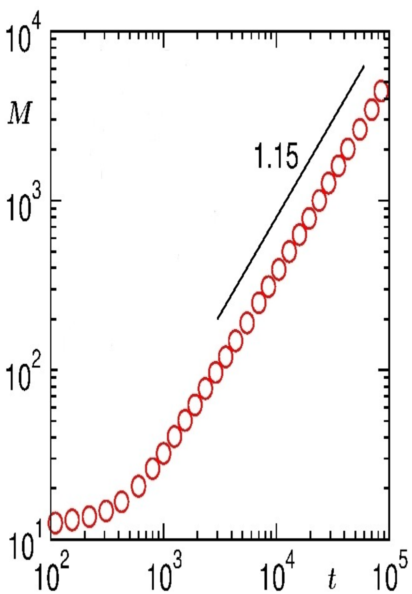
facts from molecular dynamics simulation

$\ell \sim t^{1/3}$ is accidental. Obtaining length via standard procedure followed in phase separation kinetics is meaningless, since C(r,t) does not exhibit scaling due to interesting fractal structure.

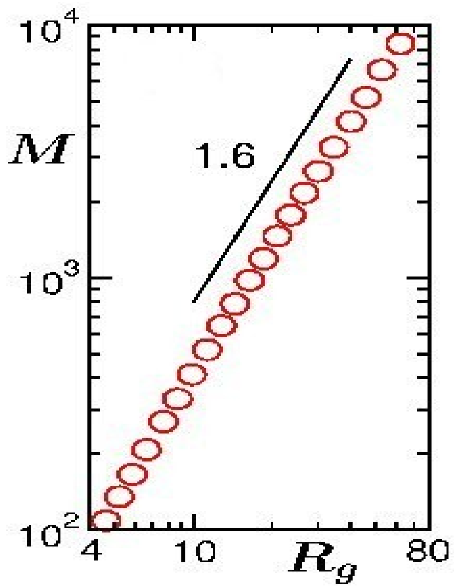


Appropriate length is the radius of gyration.

$M \sim t^{\beta}; \quad \beta = 1.15$

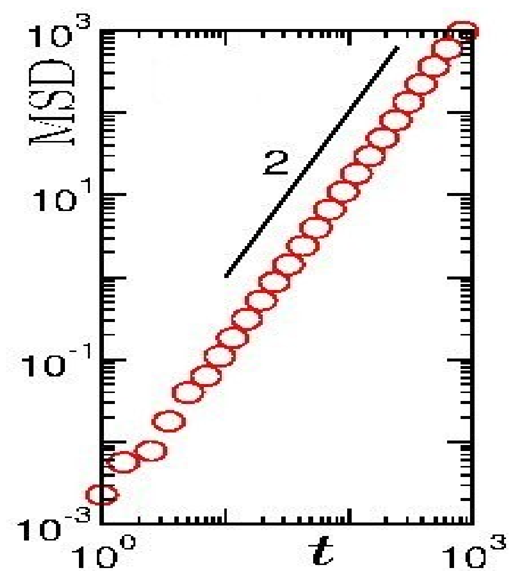


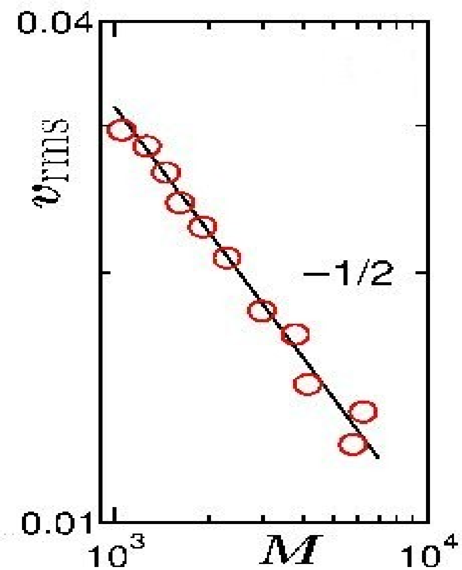
$M \sim R_g^{d_f}; \quad d_f = 1.6$



$R_g \sim t^{3/4}$

Droplets move Diffusively?





Uncorrelated ballistic motion

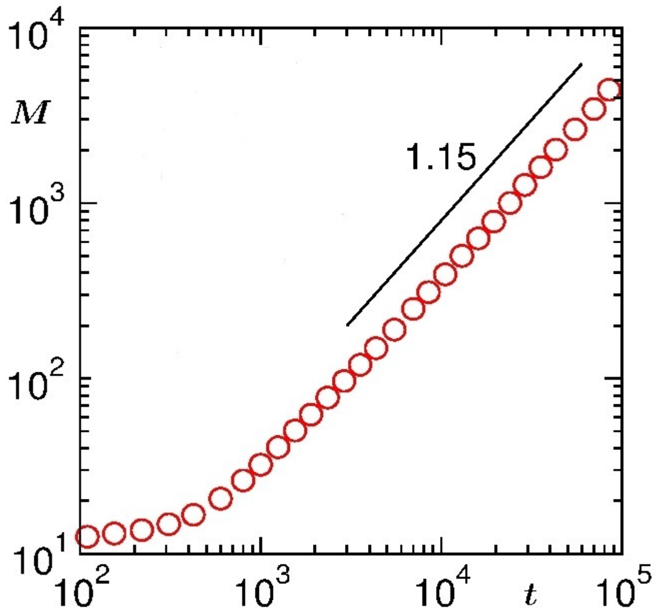
Theory of Ballistic Aggregation:

M. Smoluchowski (1916)
G.F. Carnevale, Y. Pomeau and W.R. Young, PRL (1990)
Hansen and Trizac, J. Stat. Phys. (1996)

$$\frac{dn}{dt} = -Collision-cross-section \times v_{rms} \times n^2$$

$$Collision-cross-section \sim M^{\frac{d-1}{d}} \qquad n \propto 1/M \qquad v_{rms} \sim M^{-1/2}$$

$$\frac{dM}{dt} \sim M^{\frac{d-2}{2d}} \qquad M \sim t^{\beta};\ \beta = 2d/(d+2) \qquad d=2:\ \beta=1$$

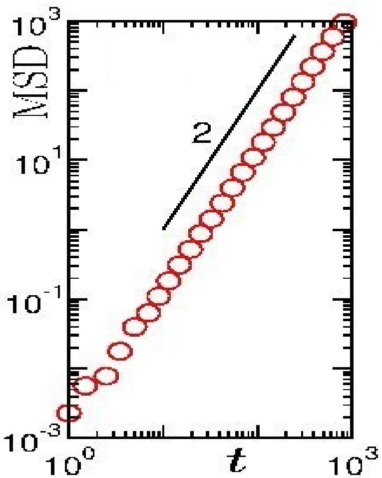


$$M \sim t^{\beta}; \quad \beta = 1.15$$

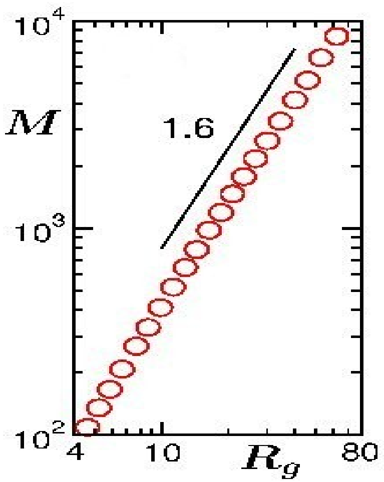
Discrepancy due to fractality?

YES.

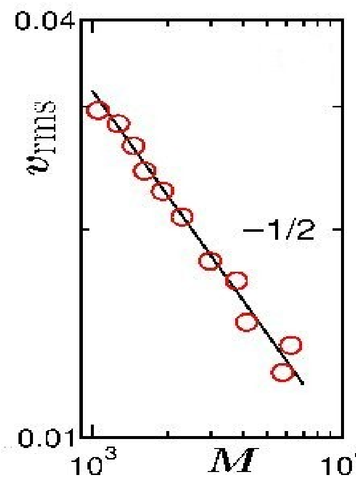
Ballistic motion



Fractal structure



Uncorrelated velocity



Problem:
Ballistic Aggregation of Fractal Objects

Theory:
$$\frac{dn}{dt} = -Collision \quad cross \quad section \times v_{rms} \times n^2$$

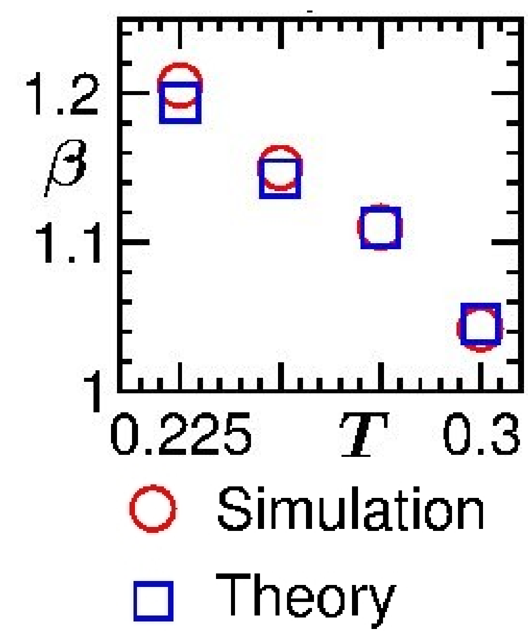
M. Smoluchowski (1916)

$$Collision-cross-section \sim R_g^{d-1} \qquad R_g \sim M^{1/d_f}$$

$$v_{rms} \sim M^{-1/2} \qquad n \sim 1/M$$

Solution: $M \sim t^{\beta}; \quad \beta = 2d_f/(3d_f - 2d + 2)$

To test the theory, i.e., dependence upon d_f, one can change it by varying temperature (T).

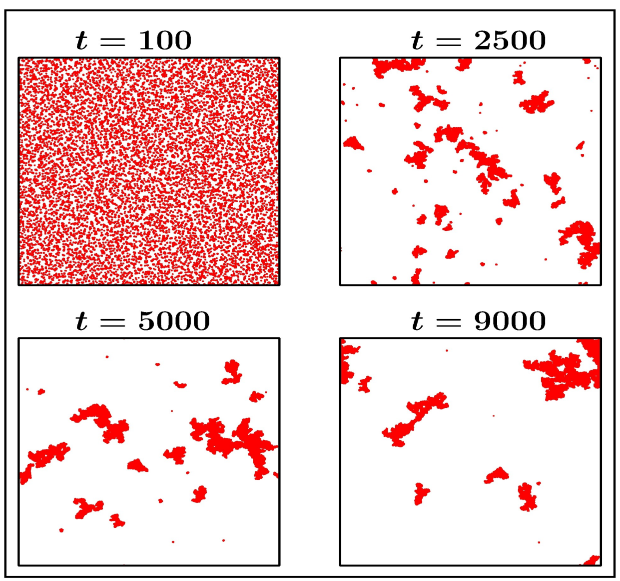


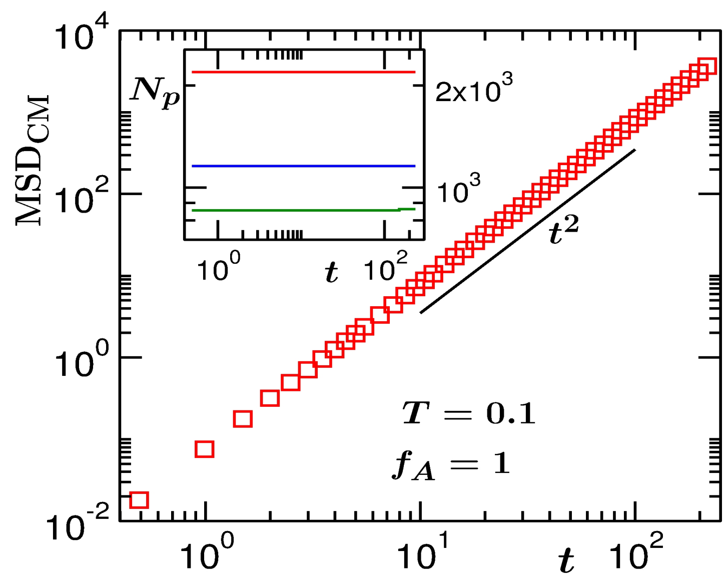
J. Midya and SKD, Phys. Rev. Lett. **118**, 165701 (2017).

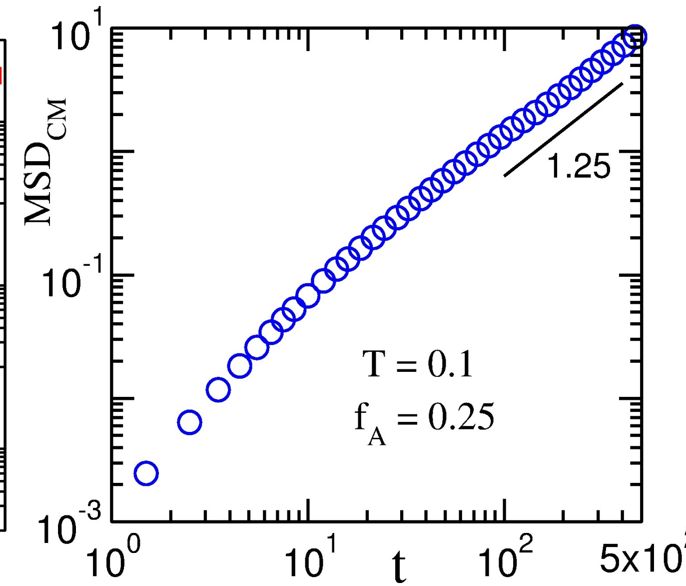
Phase separation in a Vicsek-like Active matter model

$$m\frac{d^2\vec{r}}{dt^2} = -\vec{\nabla} U_i - \gamma m \frac{d\vec{r}}{dt} + \sqrt{6\gamma k_B T m}\,\vec{R}(t) + \vec{f}_i \qquad U_i \rightarrow \text{LJ}$$

$$\langle R_{i\mu}(t) R_{j\nu}(t') \rangle = \delta_{ij}\delta\mu\nu\delta(t-t') \quad \vec{f}_i = f_A \vec{D}_N; \quad \vec{D}_N = \frac{\sum_j \vec{v}_j}{mag \sum_j \vec{v}_j}$$







By tuning the temperature and active force all types of combination of fractality and cluster mean-squared-displacements can be obtained.

Role of fractality in processes related to diffusive to ballistic coalescence can be understood.

S. Paul and SKD, to be published.

Coarsening Phenomena: Not only growth exponents

Persistence $P(t) \sim t^{-\theta}$ Bray, Derrida, Majumdar

Aging $C_{ag}(t, t_w) \sim \left(\frac{\ell}{\ell_w}\right)^{-\lambda}$ Fisher, Huse, Mazenko, Yeung, Zannetti

Pattern $C_{ag}(t, t_w) = \langle \varphi(\vec{r}, t)\varphi(\vec{r}, t_w)\rangle - \langle \varphi(\vec{r}, t)\rangle\langle \varphi(\vec{r}, t_w)\rangle$

$$C(r, t) \equiv C(r/\ell(t))$$

J. Midya, S. Majumder and SKD, J. Phys.: Condens. Matter 26, 452202 (2014)

S. Chakraborty and SKD, Europhys. Lett. 119, 50005 (2017)

N. Vadakkayil, S. Chakraborty and SKD, arXiv:1806.00312 (2018)

Scaling relations involving $\alpha, \theta, \lambda, d, d_f$

$$C(r) = r^{-p}\exp(-r/\xi)$$

$$C(r, t) \equiv r^{-p} C(r/\ell(t))$$

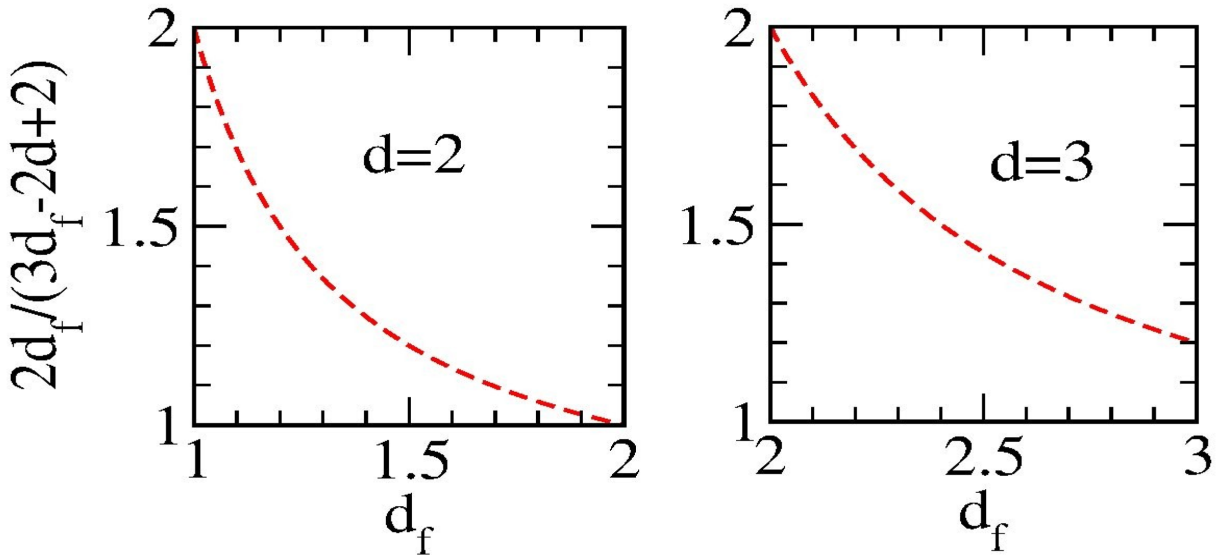
$M \sim t^{\beta}; \quad \beta = 2\mathrm{d}_f/(3\mathrm{d}_f - 2\mathrm{d} + 2) \quad \ell \sim t^{\alpha}; \quad \alpha = \theta/(d - d_f)$ Ray and Manoj

Nevertheless, universality is far weaker.

Ballistic aggregation ...

In d dimensions: collision cross section $R_g^{d-1} = M^{\frac{d-1}{d_f}}$

$$M \sim t^{\beta}; \quad \beta = 2d_f / (3d_f - 2d + 2)$$



2D: Ballistic aggregation exponent is same as Binder-Stauffer exponent for $d_f = 2.$

3D: Possiblity of exponential growth for extremely filament like strudure with $d_f = 4/3.$ But not a physical picture.

P. Cremer and H. Loewen, Phys. Rev. E (2014) – active matter context.

Summary

A general discussion on various structural and dynamical aspects of phase transitions have been provided.

In particular:

Structure and dynamics related to nucleation and growth in a single component Lennard-Jones model have been discussed.

As opposed to Ostwald ripening mechanism in solid binary mixtures or Binder-Stauffer diffusion and coalescence mechanism in liquid-liquid or vapor-liquid transitions, in vapor-solid transition for off-critical density, clusters/droplets grow via ballistic aggregation mechanism.

The observed growth law matches nicely with the theoretical picture involving the fractal dimensionality.

Despite diversity, possibilities with respect to improvement on unified understanding has been discussed.

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